IDENTIFICATION OF ORGANIC CONSTITUENTS IN AQUEOUS EFFLUENTS FROM ENERGY-RELATED PROCESSES

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The emphasis on and drive toward national energy self-sufficiency implies a very real possibility for large scale environmental degradation. There is great concern on the one hand that unabated growth in energy production and utilization will cause irreparable harm to the environment and on the otherhand that measures to protect the environment may further exacerbate the current supply problems faced by the energy industry. It is generally recognized that the nation must use coal and oil-shale over the next few decades at a rate of activity which will double or triple our current levels (1).

Prior to this report a paucity of information was available on the individual volatile organic species and their quantities in aqueous samples from energy-related processes. Characterization of energy-related effluents for volatile and semi-volatile organic components is necessary if we are to understand the energy recovery process itself as well as its environmental impact.

The development and application of capillary gas-liquid chromatography/mass spectrometry/computer (glc/ms/comp) and gas chromatography/Fourier Transform-infrared/computer (gc/ft-ir/comp) methods for characterizing and quantifying volatile and semi-volatile organics in aqueous samples from energy-related processes is described here.

EXPERIMENTAL PROCEDURES

Sampling Methods--One-liter glass amber containers were cleaned with dilute HCl, deionized-distilled water and then heated to 450°C for 2 hr. Teflon® -lined screw caps were used.

Product water from an in situ coal gasification experiment in Hanna, WY (Hanna II, Phase II, Laramie Energy Research Center, Laramie, WY) was obtained from a high temperature product stream using an ethylene glycol-cooled stainless steel condenser system. A 24 hr composite was collected in a sump, the product water and tar separated, and shipped to the laboratory. Samples were chilled to 4°C until processed.

Sample Preparation--Volatile organics were recovered from aqueous samples using previously developed methods (2-9). A 3-100 ml aqueous sample was diluted to 100 ml with deionized-distilled water, and purged with Helium in an all glass vessel (Fig. 1). The He was passed through a short glass condensor to remove water vapor and the volatiles were trapped on a 1.5 x 8.0 cm bed of Tenax GC (2,6-diphenyl-p-phenylene oxide, Applied Sci. Lab., State College, PA, 35/60 mesh). Tenax GC cartridges were prepared as previously described (10,11). Organic volatiles were purged from the sample at 60°C with a 25 ml/min He flow for 90 min. After purging, the Tenax GC cartridge was dried over 1 g $CaSO_4$ for 2 hr in a sealed Kimax® culture tube. Samples were stored at -20°C until analysis time.

Semi-volatile organics not quantitatively recovered by the above procedure were extracted from aqueous samples using Freon-TF® (Ashland Chem. Co., Raleigh, NC). Freon-TF® was purified through a florisil column prior to its use. For extraction of neutral and basic compounds, the pH was adjusted to >11 and the aqueous sample (100 ml) was partitioned four times with 100 of Freon-TF. Organic phases were combined and the organic bases extracted with 100 ml 1N HCl (F-2). The organic phase was concentrated to 2.0 ml in a Kuderna-Danish (K-D) apparatus and then to 300 µl under a slow N_2 stream. The fraction containing neutral compounds (NE) was submitted directly to instrumental analysis. The aqueous acid layer (F-2) was adjusted to pH 12 with 5N NaOH and extracted four times with 100 ml of Freon-TF®.

Freon-TF® fractions were combined, concentrated to a 2 ml in a K-D apparatus and then to 300 µl under a slow N_2 stream (B).

The original alkaline solution (F-1) was adjusted to pH 4 with 5N HCl and partitioned four times with 100 ml Freon-TF®. Organic phases were combined and concentrated to 300 µl as above (A).

Fractions containing organic acids (A) were treated with 200 µl of CH_2N_2 in diethyl ether (12) and analyzed directly by glc/ms/comp and gc/ft-ir/comp. Organic bases (B) were treated with 100 µl perfluoropropionic anhydride (PFPA, Pierce Chem., Rockford, IL) for 1 hr @ 45°C. The PFPA was neutralized with 100 µl 5% $NaHCO_3$ and the organic layer was examined by glc/ms/comp.

Instrumental Methods--Volatile organics were thermally recovered and analyzed by gc/ms/comp using a previously described inlet manifold (8-11) shown in Figure 2. Table 1 presents the instrumental parameters employed. In a typical thermal desorption cycle, a Tenax GC cartridge was placed in the preheated chamber (270°C) and the helium passed through the cartridge (∿20 ml/min) to purge the desorbed vapors into the liquid N_2 cooled Ni capillary trap. This operation was conducted with the valve in position "A" (Fig. 2). After 4 min of thermal desorption, the six-port valve (Valco Inst. Inc., Houston, TX) was rotated to position "B" (Fig. 2). The capillary trap temperature was raised from -196° to 220°C in 3 sec and the He carrier gas carried the vapors onto an OV-101 support coated open tubular column (SCOT). The SCOT's were prepared by a previously reported method (11).

Table 1. Operating Parameters for GLC-MS-COMP System

Parameter	Setting	Parameter	Setting
Inlet-manifold		MS	
desorption	270°C	scan range	m/e 20 → 300
valve	220°C	scan rate,	
capillary trap - min.	-195°C	automatic-cyclic	1 sec/decade
max.	220°C	filament current	300 µA
desorption time	4 min	multiplier	6.0
		ion source vacuum	∿4 x 10^{-6} torr
GLC			
100 m SCOT OV-101	20-240°C, 4/C° min		
50 m SCOT Carbowax 20 M	80-240°C		
carrier (He)	∿3 ml/min		
separator	240°C		

Semi-volatile organic compounds (3-5 µl) as neutrals, methylated acids and derivatized bases were also analyzed using the inlet manifold in the splitless injection mode (13). A Carbowax 20 M SCOT was employed.

Mass cracking patterns were automatically and continuously acquired throughout the chromatographic run using a Varian MAT CH-7 mass spectrometer/620L computer system (i.e., 30 eV) equipped with a Diablo Dual Disk system, Statos 3185 recorder, and a Magnetic Tape Deck.

Nicolet 7091 (Nicolet Inst., Madison, WI) and Digilab FTS-20 (Digilab Inc., Cambridge, MA) gc/ft-ir/comp systems were used for acquiring infra-red spectra (0.5 sec/scan, 8 cm^{-1}) of semi-volatile organic acids. Gas chromatography was performed on a 1/8 in x 9 ft S.S. column packed with 10% Carbowax 20 M on 80/100 mesh Chromosorb W(HP).

Radiolabeled Recovery Studies--To determine the percent recovery for the volatile and semi-volatile purification procedures, radiolabeled compounds were employed. Toluene[Ring-^{14}C, 4.0 µC/mM], benzene [^{14}C, 13.6 µC/mM], phenol [^{14}C (U), 10.7 µC/mM], acetone [2-^{14}C, 6.5 µC/mM], dimethylbenzanthracene-^{14}C, phenyl ethyl amine·HCl-^{14}C, and 3-amino-1,2,4-triazole were purchased from New England Corporation, Boston, MA. Acetonitrile [1-^{14}C, 14.9 µC/mM] and n-hexanoic acid [1-^{14}C, 58 µC/mM] were purchased from Amersham Searle, Corp. Plains, IL.

Radioisotopes were diluted in distilled-deionized water to a few μC/ml. Samples were spiked with radiolabeled compounds prior to purification. The radioactivity on the solid sorbent Tenax and in liquid fractions from the liquid-liquid (LL) fractionation scheme was determined with a Packard Tricarb 3375 liquid scintillation spectrometer. To the fraction was added 15 ml of scintillation fluid and the sample was counted until a standard error of 2.5 was obtained. The scintillation fluid contained 18 g of Omnifluor®, 1 ℓ of Triton-X® and 2 ℓ of toluene. Observed radioactivity was corrected for quenching by the external standard ratio method and by adding known quantities of radiolabeled compounds to each of the fractions to be counted. All counts were converted to disintegrations, per minute.

Data Interpretation--Identification of resolved components was achieved by comparing the mass cracking pattern of the unknown to an eight major peak index of mass spectra (14). Individual difficult unknowns were submitted to the Cornell University STIRS and PBM systems and/or the EPA MSSS System (Cyphernetics) for identification. When available, authentic compounds of the tentatively identified components were obtained and chromatographed under identical conditions on the OV-101 or Carbowax 20 M glass capillary column. The elution time and temperature for the authentic compounds was compared to the unknown in order to establish further the identity of the component.

Identities were assigned on a graded scale. When observed mass spectra matched library spectra and/or indexes of tabulated spectra and the elution time and temperature corresponded with that of an authentic compound identification was positive. Confirmation was also provided by infra-red spectra, particularly for isomeric forms. When the isomeric form could not be distinguished, the name of the compound as an isomer was indicated. In other cases, only an empirical formula could be assigned since the mass cracking patterns of isomers were very similar and the retention index could not be determined for all of the isomers since all the authentic compounds were not available. In some cases, a tentative identification was assigned when the mass cracking pattern yielded a "similar" match, and no retention index was available for that compound.

Quantification of Volatiles and Semi-volatiles--The volatile and semi-volatile compounds were quantitated by glc/ms/comp utilizing the total ion monitor and, when necessary, mass fragmentography. In order to eliminate the need to obtain complete calibration curves for each compound for which quantitative information was desired, we used the method of relative molar response (RMR) factors. This method required information on the exact amount of reference standard added and the relationship of the RMR for the unknown to the RMR of the standard. The method of calculation was as follows:

$$RMR_{unknown/standard} = \frac{A_{unk}/Moles_{unk}}{A_{std}/Moles_{std}} \quad 1) \qquad \text{or} \qquad RMR_{unk/std} = \frac{A_{unk}/g_{unk}/GMW_{unk}}{A_{std}/g_{std}/GMW_{std}} \quad 2)$$

A = Peak area
g = number of grams present
GMW = gram molecular weight

Thus, in the sample analyzed:

$$g_{unk} = \frac{A_{unk} \cdot GMW_{unk} \cdot g_{std}}{A_{std} \cdot GMW_{std} \cdot RMR_{unk/std}} \quad 3)$$

The value of RMR is determined from at least five independent analyses.

Reference standards, hexafluorobenzene (HFB) and perfluorotoluene (PFT), were added (200 ng) after the volatile organics were trapped on the Tenax GC cartridge. On an OV-101 glass capillary they did not interfere with the analysis of unknown compounds. Nitrobenzene-d_5 (200 ng) was used for quantification of semi-volatile organic compounds.

Quality Control Procedures--To monitor the possible introduction of impurities from the materials used in the purification procedures, we used a reagent and glassware

control that incorporated blanks. High quality commercial reagents and solvents were available, but the quality was somewhat variable. Freon-TF® which was used for extraction of semi-volatiles was concentrated by a factor of 100 to determine the potential contaminants. This procedure was repeated with each new lot of Freon-TF®. Deionized-distilled water was obtained by passing tap water through an ion exchange bed (No. 3508B, Corning Glass, Corning, NY), and a carbon adsorption cartridge (Hydro•Purge, Durham, NC) to remove trace elements and organic constituents, respectively, prior to its distillation. Water which was used for the dilution of the liquid samples was independently assessed for background contamination by subjecting it to the entire analytical procedure including gc/ms analysis. All glassware was cleaned with Isoclean (Isolab, Akron, OH), rinsed with deionized-distilled water, HCl, deionized water and then heated to 450°-500°C to remove traces of organic compounds.

Instrumental control was employed to insure that the entire system was calibrated and properly working. A 12 component reference mixture was used to evaluate the performance of the entire high resolution gc/ms/comp system. The mixture contained non-polar, semi-polar and polar substances.

RESULTS AND DISCUSSION

Radiolabeled Recovery Studies--(Volatiles)--Recovery of ^{14}C-acetone, acetonitrile, benzene and toluene from energy-related samples (in situ coal gasification) was determined. For compounds which are highly soluble in water, e.g., acetonitrile, the recovery by this method was very low (∿10%). Recovery of ^{14}C-labeled acetone was ∿50%. On the other hand, the recovery of hydrocarbons, aromatics (benzene and toluene) and alkyl-aromatics was ≥80%. These observations were consistent with previously reported data (2-4).

In general, the purging of volatile organics from an aqueous medium utilizing an inert gas was quantitative for compounds with boiling points ≤210° and <2% solubility and for compounds with boiling points of <150° with a solubility of <10% in water. The percentage recoveries which were determined for ketones, aliphatic and aromatic hydrocarbons, thiophenes and aldehydes, was used for calculating concentrations of sample components.

(Semi-Volatiles)--Percent recovery for selected radiolabeled compounds added to aqueous samples was also determined for the LL extraction method (Table 2). The observed percentage recovery represents an overall average prior to instrumental analysis. For toluene and dimethylbenzanthracene, essentially quantitative recovery was observed for the LL extraction method and the K-D concentration steps. Quantitative recoveries for palmitic, hexanoic, and benzoic acids and phenol were also obtained. However, the highly water soluble butyric acid was not recovered. It was concluded that, for quantification of acids utilizing this LL extraction method, reliable data could be obtained for acids containing four or more methylene units.

Two bases were also subjected to the LL extraction method to determine its efficiency. A recovery of ∿68% was observed for phenyl ethyl amine in the basic fraction with only minor amounts remaining in several other fractions. In contrast, the water soluble amine, 3-amino-1,2,4-triazole, could not be quantitatively extracted.

From these data, it was concluded that moderately water soluble and/or moderately volatile compounds could be recovered by this LL extraction technique and retained in the receiver of the K-D apparatus. These data were used for calculating the quantities of the individual semi-volatile acids, bases, and neutral compounds in the energy samples.

Quantification by GC/MS/COMP Using Relative Molar Response (RMR) Factors--The RMR of several aliphatic and aromatic compounds based upon the total ion current monitor are presented in Table 3. As can be seen from these data, similar RMR's for the aliphatic hydrocarbons allow calculation of an "average RMR" for this chemical class. Thus, other compounds in the same chemical class for which authentic standards were not available could be quantified.

Table 2. Percent Recovery of Selected Radiolabeled Compounds Using Liquid/Liquid Extraction Method

Radiolabeled Compound	Fraction					
	Neutral (NE)	Acid (A)	Base (B)	H_2O/H^+ [a]	H_2O/OH^- [b]	Total (Organic Phase)
Toluene	76 ± 9%	0.8 ± 0.4%	1.2 ± 0.6%	1.5 ± 1.0%	0%	79.5%
Dimethylbenzanthracene	83 ±12%	3.0 ± 1.0%	0%	0%	0%	86.0%
Palmitic acid	31 ± 4%	80 ± 8%	0%	0%	0%	111.0%
Hexanoic acid	0%	75 ± 5%	0%	24 ± 3%	0%	75.0%
Benzoic acid	0%	54%	1.5%	45%	0%	55.5%
Butyric acid	0%	0%	0%	87 ± 13%	0%	0%
Phenol	0%	53 ± 3%	0%	46 ± 4%	0%	53%
Phenylethylamine	3 ± 2%	2 ± 1%	68 ± 7%	11 ± 3%	4 ± 2%	73.0%
3-Amino-1,2,4-triazole	0%	0%	0%	85 ± 14%	0%	0%

[a] Remaining after extraction of acidic solution.
[b] Remaining after extraction of basic solution.

Table 3. Examples of Relative Molar Response (RMR) Factors for Several Compounds Based Upon Total Ion Current Monitor

Compound	PFB[a]			PFT[a]		
	RMR	Var.[b]	S.D.[b]	RMR	Var.	S.D.
n-Heptane	1.39	0.150	0.39	1.66	0.080	0.29
n-Nonane	1.85	0.020	0.14	2.04	0.008	0.09
n-Undecane	1.71	0.048	0.22	1.94	0.016	0.12
n-Tridecane	1.31	0.130	0.36	1.44	0.110	0.34
2-Pentanone	2.84	0.260	0.41	2.94	0.060	0.240
2-Ethylfuran	2.59	0.230	0.48	2.68	0.100	0.320
Toluene	2.38	0.020	0.15	2.48	0.110	0.33
Cumene	1.56	0.050	0.22	1.76	0.026	0.16
1,3,5-Trimethylbenzene	1.48	0.050	0.22	1.63	0.037	0.19
1,2,4-Trimethylbenzene	1.47	0.025	0.16	1.47	0.006	0.08
1,2,3-Trimethylbenzene	1.26	0.040	0.19	1.45	0.013	0.11
o-Xylene	2.90	0.170	0.42	2.33	0.200	0.41
Anisole	1.77	0.290	0.54	2.14	0.040	0.20
Acetophenone	1.48	0.040	0.20	1.79	0.007	0.08
2-Methylbenzofuran	1.46	0.003	0.06	1.32	0.030	0.18
Indan	1.54	0.024	0.16	1.76	0.027	0.16
m-Tolualdehyde	1.56	0.020	0.15	1.54	0.003	0.06
o-Ethylaniline	1.62	0.170	0.41	1.28	0.060	0.25

[a] PFB = perfluorobenzene, PFT = perfluorotoluene which were external standards.
[b] Var. = statistical variance, S.D. = standard deviation.

Many additional RMR's not presented in this table were also determined and calculated. The RMR factors for ketones, aldehydes, thiophenes, ethers, amines, anilines, acids, etc. were determined for those compounds which were commercially available and an "average RMR" value for each chemical class was used for estimating the concentrations of compounds appearing in the energy samples for which authentic standards were not available.

Table 4 presents selected examples of RMR factors based upon fragment ions. The RMR factors were determined for two ions utilizing mass fragmentography, and the concentration of each compound in the unknown sample was calculated. As for the RMR's based upon the total ion current monitor, the RMR factors for selected fragment ions were determined for those authentic compounds which were commercially available and in those cases where authentic compounds were not available, an "average RMR' value was calculated for each homologous series.

Table 4. Examples of Relative Molar Response Factors[a] for Several Compounds Based Upon Selected Fragment Ions

		1st Ion		2nd Ion	
Compound	MW	m/e (I)	RMR	m/e (I)	RMR
Toluene	92	91 (100)	2.37	64 (13)	0.66
o-Xylene	106	105 (27)	3.46	51 (10)	0.39
Anisole	108	108 (100)	1.19	65 (76)	1.30
Acetophenone	120	105 (100)	1.97	120 (29)	1.27
Naphthalene	128	128 (100)	1.92	51 (12)	0.18
2-Pentanone	86	43 (100)	1.98	57 (26)	0.14

[a]RMR values were calculated relative to m/e 186 (100) for the external standard, HFB.

Mass Fragmentography--The technique of mass fragmentography was utilized for the quantification of volatile and semi-volatile organics when inadequate resolution existed for the total ion current monitor. Additional specificity was obtained with ion chromatograms for the individual components. Even though high resolution glass capillary columns (SCOT's) were used for effecting the resolution of the components in each mixture, the separation efficiency of the capillaries was inadequate for obtaining baseline resolution for every constituent in the sample. Since it was impractical to utilize very high resolution capillaries, e.g. wall-coated open tubular (capacity too low) or very long SCOT capillaries, we chose the mass fragmentographic technique to obtain sufficient resolution for quantification of the individual species.

Figure 3 depicts a mass fragmentogram for several selected ions for the volatile organics in product water (13L) from an in situ coal gasification experiment. Peaks labeled 1 (m/e 67), 2 and 3 (m/e 114), 4 (m/e 71) and S (m/e 186) represent the compounds pyrrole, n-octane, 2-heptanone and PFT, respectively. Additional ion chromatograms were also obtained for this and other samples which allowed the quantitation of essentially all of the components that were identified.

GC/FT-IR/COMP--The acid fraction of an aqueous sample was also analyzed by gc/ft-ir/comp. The flame ionization chromatogram obtained simultaneously with ir spectra is shown in Figure 4. Infra-red spectra for peaks 6, 8, 10, 12 and 14 in Figure 4 confirmed these compounds as methyl benzoate, methyl hexanoate (Fig. 5), methyl heptanoate, methyl octanoate and methyl nonanoate, respectively (15,16). Figure 6 is an ir spectrum of phenol which had been also identified by gc/ms/comp. The broad peak from 300-3500 cm^{-1} due to molecular hydrogen bonding observed in condensed phase spectra (15) is absent in this gas phase system. The two peaks between 1175-1300 cm^{-1} represent symmetric and asymmetric CO stretching bands. In condensed phase spectra, this is a broad single band (15). Peaks 18, 22, and 23 were identified as methyl-m-toluate, 3,5-dimethylphenol and o-cresol, respectively after examining their ir spectra.

Sample Composition--Tables 5 and 6 present the volatile and semi-volatile organics characterized and quantified in an aqueous sample from in situ coal gasification

Table 5. Volatile Organics in Produced Water (-13L) From Well 5-6 In Situ Coal Gasification (LERC, ERDA)

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound	ppb
1	42	CO_2	NQ
2	45	carbonyl sulfide	NQ
2A	48	1-butene	NQ
3	49	n-butane	NQ
6	61-3	acetone	1243±0
7	61-4	acetonitrile	620±60
9	70	carbon disulfide	NQ
11	77	propionitrile	382±47
13	82	methyl ethyl ketone	645±33
15	88	isobutyronitrile	53±16
16	92	perfluorotoluene (e[illegible])	-
16A	96	methyl isopropyl ketone	55±5
17	98	benzene	607±6
18	100	n-butyronitrile	267±13
18A	101	thiophene	620±6
19	104	2-pentanone	124±111
20	106	3-pentanone	55±0
21	112	α-methylbutyronitrile	32±9
22	115	N-methylpyrrole	2±0
23	116	4-methyl-2-pentanone	148±80
24	118	pyrrole	208±21
25	121	n-pentylnitrile	53±0
26	123	toluene + methylthiophene + pyridine	556±200 2222±4
27	124	3-hexanone	27±8
28	125	cyclopentanone	32±9
29	127	n-octane	1±0
31	133	sulfur compound (?)	NQ
32	135	3-methylpyrrole	46±4
33	138	2-methylcyclopentanone + 2-metbylpyrrole	101±10 24±2
34	140	methylpyridine isomer	120±11
35	141	C_9H_{20} isomer	17±7
36	143	ethylbenzene	222±27
36A	144	C_8H_{16} isomer	4±0.3
37	146	p-xylene	561±60
38	148	2,4-dimethylthiophene	15±0
39	149	2-heptanone	5±0
40A	151	2,3-dimethylthiophene	52±3
40	152	styrene + C_9H_{18} isomer	118±11
41	153	o-xylene	472±37
42	155	n-nonane + dimethylpyridine isomer	39±12 74±15
43	157	dimethylpyridine + C_9H_{18} isomers	417±7
44	158	dimethylpyrrole isomer	7±1
45	160	isopropylbenzene	11±0
	160	$C_{10}H_{20}$ isomer	209±7
46	161	$C_{10}H_{18}$ isomer	5±0
47	163	C_3-alkyl cyclohexane isomer	57±2
48	165	$C_{10}H_{22}$ isomer	27±8
49A	167	$C_{10}H_{20}$ isomer	11±5
49	168	n-propylbenzene	28±3
	169	$C_{10}H_{20}$ + trimethylcyclohexane isomers	96±14
50	170	m-ethyltoluene	184±16
51	170	p-ethyltoluene	61±7
52	171	2-isopropylthiophene	38±16
52A	172	$C_{10}H_{20}$ + $C_{10}H_{22}$ isomers	21±0.3
53	172	trimethylpyridine isomer	40±2
53A	173	cyanobenzene	44±5
54	175	o-ethyltoluene	67±17
56	177	$C_{10}H_{20}$ isomer	30±2
57A	178	α-methylstyrene + $C_{10}H_{20}$	349±42
57	180	1,2,4-trimethylbenzene + n-decane + benzofuran	267±27 111±16
58	182	$C_{10}H_{20}$ + trimethylthiophene isomers	11±0.6 15±0
58A	184	C_4-alkyl benzene isomer	6±2
59	186	C_4-alkyl benzene isomer	9±3
60	187	C_3-alkyl pyridine isomer	15±3
61	189	indan	334±33
61A	190	phenol	NQ
62	181	indene	272±32
63	192	C_4-alkyl benzene isomer	71±20
63A	193	C_4-alkyl benzene isomer	20±7
64	193	$C_{11}H_{24}$ isomer	57±5
65	195	C_4-alkyl benzene isomer	22±11
66	197	C_4-alkyl benzene isomer + o-cresol	NQ
67	198	$C_{11}H_{22}$ + C_4-alkyl benzene isomers	95±32
68A	201	C_5-alkyl benzene isomer	139±21
69	203	methylbenzofuran isomer	28±4
70	205	p-cresol	NQ
71	206	C_4-alkyl benzene isomer	12±6
71	207	dimethylindan isomer	47±3
72	208	C_5-alkyl benzene isomer	69±13
73A	209	C_5-alkyl benzene isomer	12±1
73	210	methylindan isomer	126±15

(continued)

Table 5 (cont'd)

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound	ppb
73B	211	$C_{12}H_{26}$ + methylindene isomers	184±164
74A	212	C_5-alkyl benzene isomer	12±1
74	212	$C_{10}H_{12}$ + C_4-alkyl benzene isomers	63±15
75	213	methylindene isomer	196±31
76	215	dimethylphenol + C_5-alkyl benzene isomers	NQ
76A	216	C_5-alkyl benzene isomer	T
	217	dimethylindan isomer	T
77	218	1-dodecene	13±5
78	200	n-dodecene	86±8
79	221	naphthalene	640±32
79A	222	dimethylindan + C_6-alkyl benzene isomers	162±15
		benzothiophene	42±5
			118±6
80	224	dimethylbenzofuran isomer	148±22
81	225	$C_{12}H_{16}$ + C_6-alkyl benzene isomers	56±4
82	227	$C_{11}H_{14}$ isomer	11±0
83	228	dimethylindene + C_6-alkyl benzene isomers	17±7
	229	trimethylindan isomer	22±0
84	230	$C_{13}H_{28}$ isomer	NQ
85	231	$C_{11}H_{14}$ + C_6-alkyl benzene isomers	NQ
86	232	dimethylindene + $C_{14}H_{30}$ isomers	50±10
87	233	dimethylindan + dimethyl-indene isomers	128±11
88	235	1-tridecene + trimethyl-indan isomer	12±0.7
			94±7
89	237	n-tridecane	222±11
90	238	trimethylindan isomer	115±15
92	240	α-methylnaphthalene	162±16
93	isothermal	β-methylnaphthalene	345±7
94		2-isopropylbenzimidazole (tent.)	25±2
95		$C_{13}H_{18}$ isomer	11±0
96		$C_{14}H_{30}$ isomer	19±4
97		n-heptylbenzene	26±5
98		$C_{15}H_{32}$ isomer	21±6
99		1-tetradecene	47±4
99A		biphenyl	114±12
100		n-tetradecane	129±14
101		$C_{13}H_{18}$ isomer	16±7
102		ethylnaphthalene isomer	39±9
103		dimethylnaphthalene isomer	195±17
104		dimethylnaphthalene isomer	100±12
105		dimethylnaphthalene isomer	135±52
106		$C_{16}H_{32}$ isomer	26±11
107		dimethylnaphthalene isomer	47±14
108		ethylnaphthalene isomer	69±21
109		n-pentadecane	T
111		acenaphthene	612±9
112		isopropylnaphthalene isomer	
113		$C_{18}H_{28}$ isomer (tent.)	T
114		$C_{14}H_{20}$ isomer	31±5
115		trimethylnaphthalene isomer	7±1
117		C_3-alkyl naphthalene isomer	5±1
119		C_3-alkyl naphthalene isomer	7±0
119A		methyl acenaphthene isomer	15±3
120		C_3-alkyl naphthalene isomer	T

Table 6. Semi-Volatile Organics in Produced Water (-13L) From Well 5-6 In Situ Coal Gasification (LERC, ERDA)

Elution Temperature (°C)	Compound	ppb
97	C_5H_{12} isomer	NQ
98	methyl ethyl ketone	NQ
99	methyl isopropyl ketone	NQ
99	propanal	NQ
100	benzene	156
101	n-butanal	NQ
101	2-pentanone	1170
101	n-butyric acid	90
102	4-methyl-2-pentanone	80
103	isopentanoic acid	170
103	3-methyl-2-pentanone	110
104	n-propionitrile (tent.)	130
104	$C_5H_{10}O_2$ carboxylic acid	42
105	toluene	90
105	3-hexanone	T
106	$C_5H_{10}O_2$ carboxylic acid	T
106	2-methyl-1,3-dioxane	T
107	2-hexanone	140
107	n-pentanoic acid	1060
107	2-methylpentanoic acid	260
108	α-methylbutyronitrile	T
109	n-butyronitrile	84
110	$C_7H_{14}O$ isomer	T
111	ethylbenzene	T
112	p-xylene	140
112	isohexanoic acid	190
113	C_2-alkyl benzene isomer	T
114	unknown	NQ
116	n-hexanoic acid	1470
117	o-xylene	66
118	n-pentylnitrile	T
119	cyclopentanone	48
119	methylcyclopentanone + n-propylbenzene	T

(continued)

Table 6 (cont'd)

lution Temperature (°C)	Compound	ppb	Elution Temperature (°C)	Compound	ppb
120	$C_8H_{16}O_2$ carboxylic acid	T	158	benzofuran	90
121	2-n-pentylfuran	T	189	d_5-nitrobenzene (ex)	
122	$C_6H_{10}O$ isomer	48	201	aniline	3460
123	$C_8H_{16}O_2$ carboxylic acid	78	204	dimethylphenol isomer	990
124	isoheptanoic acid	30	215	phenol + cresol isomer	270000
128	n-heptanoic acid	870	217	dimethylphenol isomer	600
132	n-butylbenzene	18	220	ethylphenol isomer	18
136	anisole	100	221	dimethylphenol isomer	60
141	n-octanoic acid	110	222	cresol isomer	850
145	n-pentylbenzene	T	223	cresol isomer	10200
149	p-cresyl methyl ether	18	227	C_3-alkyl phenol isomer	170
153	dimethylpyridine + methylethyl-pyridine isomer	12	227	C_3-alkyl phenol isomer	180
			229	C_3-alkyl phenol isomer	830
156	$C_{10}H_{12}$ isomer	T	231	dimethylphenol isomer	7800
156	indene	96	235	C_3-alkyl phenol isomer	6
157	pyrrole	270	237	C_2-alkyl phenol isomer	8100

(Hanna, WY). Many compounds containing sulfur (thiophenes, mercaptans, sulfides, etc.), nitrogen (nitriles, pyridines, aniline, etc.), oxygen (aldehydes, ketones, acids, phenols, etc.) were present. Many hydrocarbons and aromatic compounds were also identified.

The techniques of glass capillary gc/ms/comp and gc/ft-ir/comp were found to be powerful complementary tools for the characterization of energy samples when used with the described sample preparation procedures.

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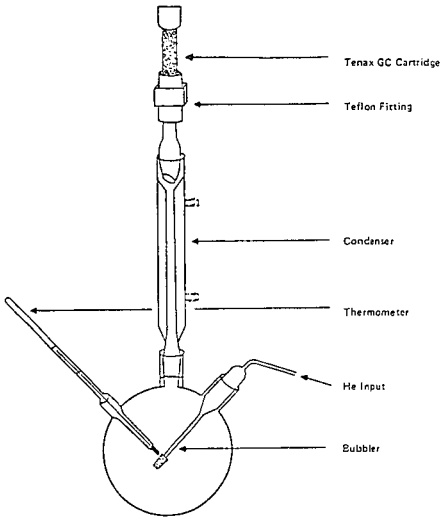

Figure 1. Purge apparatus for volatile organics.

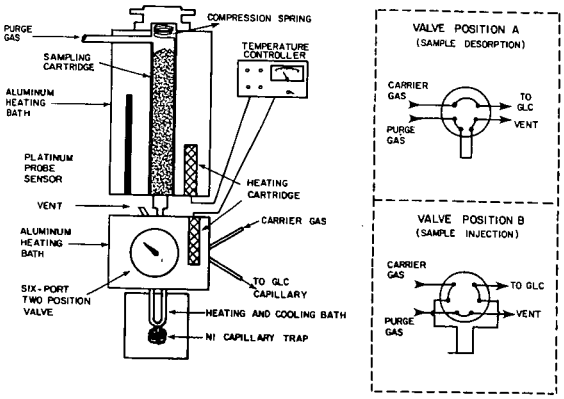

Figure 2. Inlet manifold for recovery of volatile organics from Tenax GC® cartridges.

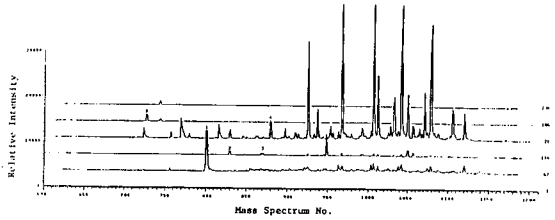

Figure 3. Mass fragmentograms of aqueous sample from in situ coal gasification.

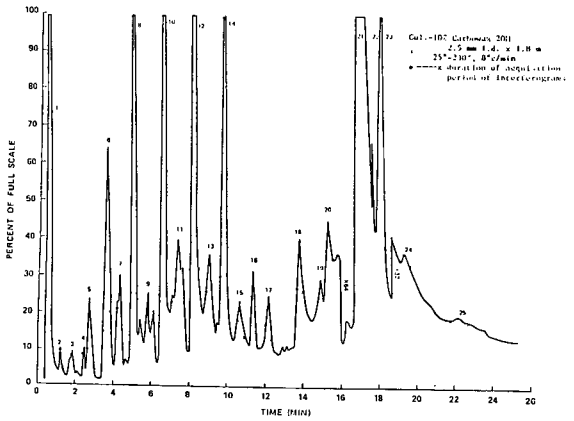

Figure 4. Flame ionization chromatogram for organic acid fraction obtained during ir spectral acquisition.

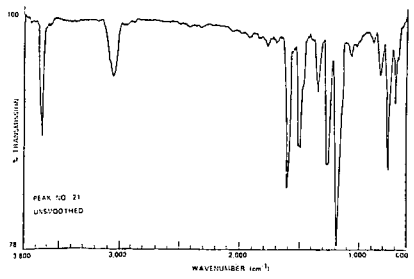

Figure 5. Ir spectrum of peak No. 8 in Figure 4.

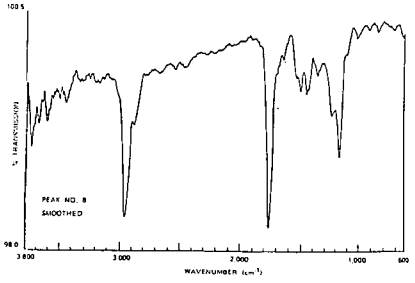

Figure 6. Ir spectrum of peak No. 21 in Figure 4.